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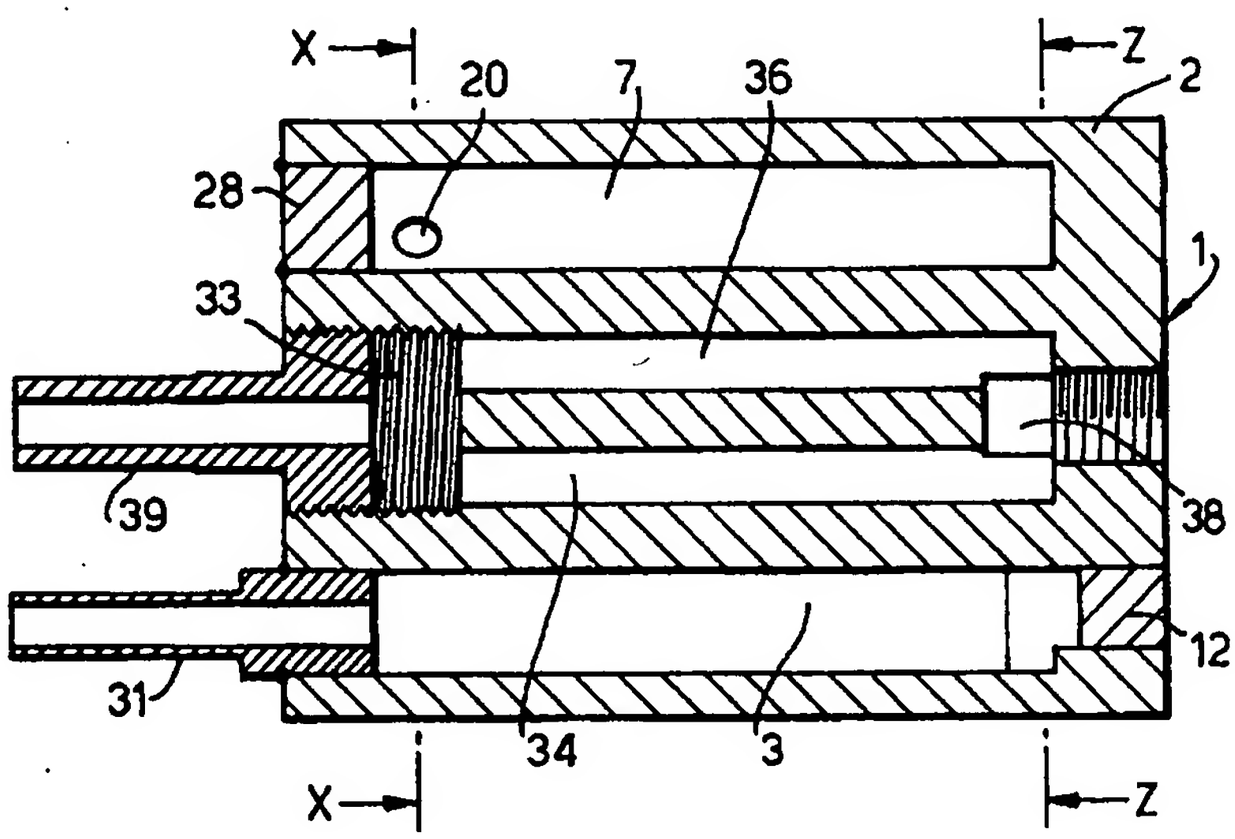
(54) Title: CATALYTIC REACTOR



(57) Abstract

A catalytic reactor (1) comprises a housing (2) of heat conducting material in which is located (a) a plurality of catalyst bed tubes (3, 4, 5, 6, 7, 8, 9, 10) interconnected in series and adapted to receive in each catalyst bed tube a through–flowing gas to be catalytically reacted and (b) cooling tubes (34, 35, 36, 37) adapted to receive a through–flowing coolant for controllable extraction of heat from the exothermic reaction. The housing (2) can be a solid cylinder of aluminium or other heat conducting material having the catalyst bed tubes (3, 4, 5, 6, 7, 8, 9, 10) and the cooling tubes (34, 35, 36, 37) drilled lengthwise in the cylinder. The catalytic reaction is particularly suitable for the removal of carbon monoxide from a hydrogen–containing gas by selective catalytic methanation.

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CATALYTIC REACTOR

This invention relates to a catalytic reactor for exothermic chemical reactions.

More particularly, but not exclusively, this invention relates to a catalytic reactor for purifying gas streams containing hydrogen, carbon monoxide and carbon dioxide, *eg* the removal of carbon monoxide from reformate gas mixtures.

One method of catalytically removing carbon monoxide from a reformate gas mixture is by the selective methanation of carbon monoxide to methane. Temperature control of methanation reactions is extremely important because methanation reactions are exothermic and too high a temperature results in unwanted carbon dioxide methanation. At lower temperatures, carbon monoxide methanation inhibits carbon dioxide methanation and even when there is little carbon monoxide left in the reformate, carbon dioxide methanation remains limited.

An object of the present invention is to provide a catalytic methanation reactor in which control of temperature in the catalyst bed can be achieved very accurately thus ensuring selective methanation of substantially all of the carbon monoxide in the reformate gas stream with little or no methanation of carbon dioxide.

According to the present invention, a catalytic reactor for exothermic chemical reactions comprises a housing of heat-conducting material in which is located (a) a plurality of catalyst bed tubes inter-connected in series and adapted to receive in each tube successively a through-flowing gas to be catalytically reacted and (b) one or more cooling tubes adapted to receive a through-flowing coolant for controllable extraction of heat from the exothermic reaction.

Preferably, the catalyst bed tubes are located around the cooling tube or tubes.

Further preferably, the reactor is associated with means for supplying controllable heat to the outer surface of the housing.

Suitably, the reactor of the invention has at least three catalyst bed tubes and preferably it has eight catalyst bed tubes and four cooling tubes.

Preferably, the catalyst bed tubes are inter-connected in such manner that the gas to be reacted flows through the catalyst bed tubes alternately co-current and counter-current to the coolant.

Preferably, the housing of the reactor is a solid cylinder of heat-conducting material having the catalyst bed tubes and the cooling tubes drilled lengthwise in the cylinder.

Further preferably, the heat-conducting material of the housing is aluminium, copper, stainless steel or carbon steel.

From another aspect, the present invention is an exothermic chemical reaction conducted in a catalytic reactor as claimed herein.

Suitably, the exothermic chemical reaction is the removal of carbon monoxide from a hydrogen-containing gas, *eg* a reformate gas mixture.

The catalytic reactor of the invention is particularly suitable for small scale portable applications such as portable hydrogen generation units.

A particular advantage of the reactor of the invention is that it can reduce the carbon monoxide in a reformate gas mixture from around 5vol% to below 100ppm in a single pass through the reactor.

A specific embodiment of the invention will now be described, simply by way of example, with reference to the accompanying drawings in which:

Figure 1 is a sectional front elevation of the reactor;

Figure 2 is a side elevation of the front end of the reactor;

Figure 3 is a sectional side elevation of the front end of the reactor on the line X-X;

Figure 4 is a side elevation of the rear end of the reactor;

Figure 5 is a sectional side elevation of the rear end of the reactor on the line Z-Z, and

Figure 6 illustrates the results obtained in the tests conducted under Example 3 below.

The catalytic reactor 1 is constructed from a solid aluminium cylinder 2.

Eight equispaced radially disposed tubes 3, 4, 5, 6, 7, 8, 9, 10 are drilled lengthwise in the solid aluminium cylinder 2 from the front end of the reactor for most of its length. The tubes 3, 4, 5, 6, 7, 8, 9, 10 when filled with catalyst function as one continuous catalyst bed.

Four equispaced radially disposed holes 11, 12, 13, 14 are drilled in the solid aluminium cylinder 2 from the rear end of the reactor 1 to such depth as to connect them with tubes 3, 4, 5, 6, 7, 8, 9, 10. As can be seen in Figure 5, the holes 11, 12, 13, 14 are located such that they provide connections at the rear end of the reactor 1 between certain of the tubes 3, 4, 5, 6, 7, 8, 9, 10 as follows:

(i) 3 is connected to 4;

(ii) 5 is connected to 6;

(iii) 7 is connected to 8; and

(iv) 9 is connected to 10.

Aluminium weld plugs 15, 16, 17, 18 are then welded into the holes 11, 12, 13, 14 to seal them off.

Referring now to Figure 3 of the drawings, three holes 19, 20, 21 are drilled inwards from the circumferential wall of the aluminium cylinder 2. The holes 19, 20, 21 are of such depth and are positioned such that they provide connections at the front end of the reactor 1 between certain of the tubes 3, 4, 5, 6, 7, 8, 9, 10 as follows:

(i) 4 is connected to 5;

(ii) 6 is connected to 7; and

(iii) 8 is connected to 9.

Aluminium weld plugs 22, 23, 24 are then welded into the holes 19, 20, 21 to seal them off.

The tubes 3, 4, 5, 6, 7, 8, 9, 10 are filled with catalyst and aluminium weld plugs 25, 26, 27, 28, 29, 30 are inserted into tubes 4, 5, 6, 7, 8, 9 to seal them off. Tubes 3 and 10 have gas connectors 31 and 32 inserted into them. Catalyst is retained within tubes 3 and 10 by gauzes located therein.

The cooling system of the reactor 1 is made as follows. A hole 33 is drilled axially from the front end of the reactor 1 inwards for a short distance. Four equispaced radially disposed holes 34, 35, 36, 37 of narrow diameter are drilled from the front end of the reactor 1 for almost the whole length of the reactor 1 to provide tubes for the flow of coolant through the centre of the reactor 1. A hole 38 is drilled axially inwards from the rear end of the reactor 1 for a short distance. Hole 38 is then part-threaded for more than half of its length. The hole 38 connects with the four coolant tubes 34, 35, 36, 37 so that the coolant entering the rear end of the reactor 1 through hole 38 passes down the centre of the reactor 1 by means of tubes 34, 35, 36, 37. A coolant connector (not shown) is screwed into hole 38 at the rear end of the reactor 1 and an adaptor 39 is fitted into hole 33 at the front of the reactor 1.

The arrangement of catalyst-filled tubes 3, 4, 5, 6, 7, 8, 9, 10 provides eight catalyst beds connected in series giving a total catalyst bed volume of around 61ml. The gas which is to undergo the exothermic catalytic reaction enters the reactor 1 at the front end through tube 3 and then passes in turn through each of tubes 4, 5, 6, 7, 8 and 9 and finally leaves from the front end of the reactor 1 through tube 10. The coolant enters the reactor 1 through its rear end and leaves at the front end. The arrangement is such that the gas flows through the tubes 3, 4, 5, 6, 7, 8, 9, 10 alternately co-current and counter-current to the cooling medium. A wide variety of coolants can be used, (*eg* air or water).

The reactor 1 operates on the principle of a heat exchanger. The reactor 1 can be heated to the temperatures at which the exothermic reaction commences by a heating mantle (not shown), which fits exactly around the outside of the aluminium cylinder 2. The heating mantle can be set to cut out when the required reaction temperature is reached. Thus the outer part of the reactor 1 is heated, while the inner part is cooled. This gives excellent temperature control of the reactor 1 and the catalyst beds.

Whilst the reactor described above can be used for many exothermic catalytic chemical reactions it is particularly suitable for the selective methanation of carbon monoxide in a hydrogen-containing gas, *eg* a reformate gas. Suitable methanation catalysts are supported noble metal catalysts, *eg* rhodium supported on alumina. The catalyst preferably is in the form of pellets.

There now follows some examples of the reactor being used for carbon monoxide methanation.

EXAMPLE 1

A synthetic reformate consisting of H_2 (55vol%), N_2 (24vol%), CO_2 (20vol%) and CO (1vol%) was tested. The measurements were taken at intervals of 15 minutes.

Concentrations		Conversions		
[CO] (ppm)	[H_2] (vol%)	CO (ml/min)	H_2 (ml/min)	CO_2 (ml/min)
17	51	100	775	118
18	51	100	755	109
18	51	100	726	106
17	52	100	716	105
18	52	100	699	101
18	52	100	687	98

Test Conditions

1. Total flow 10 litres/min or 600 l/hour
2. Reactor temperature 266°C.
3. Feed stream inlet temperature 160-170°C.
4. Coolant flow 27 litres/minute air.
5. Catalyst 2% Rh/Al_2O_3.

EXAMPLE 2

A synthetic reformate consisting of H_2 (55vol%), N_2 (23vol%), CO_2 (20vol%) and CO (2vol%) was tested. The measurements were taken at intervals of 15 minutes.

Reactor Temperature (°C)	Concentrations		Conversions		
	[CO] (ppm)	[H_2] (vol%)	CO	H_2	CO_2
274	181	50	196	707	25
277	47	50	197	808	44
277	43	50	197	805	40
278	32	49	197	879	56
277	31	49	197	888	62
277	31	49	197	879	58
277	34	49	197	843	52
277	34	49	197	852	51
281	30	48	197	963	18
280	30	48	197	984	84
280	30	48	197	948	79
281	30	48	197	959	79
280	30	48	197	946	77

Test Conditions:

1. Total flow 10 litres/minute or 600 litres/hour
2. Reactor temperature (see column 1).
3. Feed stream inlet temperature 160-170°C.
4. Coolant flow 24 litres/minute air.
5. Catalyst 2% Rh/Al_2O_3.

EXAMPLE 3

Figure 6 illustrates the results which were obtained using the methanation reactor to clean up the reformate of a reformer as disclosed in WO 96/00186. The Table below illustrates the average results.

	CO	CO_2	H_2	Ar	N_2	CH_4	H_2O	MeOH
		(vol%)	(vol%)	(vol%)	(vol%)	(vol%)	(vol%)	(vol%)
Inlet	3.0 vol%	18	45	0.2	20	0.2	14	0.2
Outlet	81 ppm	16.9	35.7	0.2	19.3	4.2	23-25	0*

* - no MeOH detected, therefore the concentration is smaller than 100ppm.

CLAIMS

1. A catalytic reactor for exothermic chemical reactions comprising a housing of heat-conducting material in which is located (a) a plurality of catalyst bed tubes inter-connected in series and adapted to receive in each tube successively a through-flowing gas to be catalytically reacted and (b) one or more cooling tubes adapted to receive a through-flowing coolant for controllable extraction of heat from the exothermic reaction.

2. A catalytic reactor as claimed in claim 1 wherein the catalyst bed tubes are located around the cooling tube or tubes.

3. A catalytic reactor as claimed in claim 1 or 2 associated with means for supplying controllable heat to the outer surface of the housing.

4. A catalytic reactor as claimed in any one of the preceding claims having at least three catalyst bed tubes.

5. A catalytic reactor as claimed in any one of the preceding claims having eight catalyst bed tubes and four cooling tubes.

6. A catalytic reactor as claimed in any one of the preceding claims wherein the catalyst bed tubes are inter-connected in such manner that the gas to be reacted flows through the catalyst bed tubes alternately co-current and counter-current to the coolant.

7. A catalytic reactor as claimed in any one of the preceding claims wherein the housing is a solid cylinder of heat-conducting material having the catalyst bed tubes and the cooling tubes drilled lengthwise in the cylinder.

8. A catalytic reactor as claimed in any one of the preceding claims wherein the heat-conducting material of the housing is aluminium, copper, stainless steel or carbon steel.

9. An exothermic catalytic chemical reaction conducted in a reactor as claimed in any one of claims 1 to 8.

10. A process for the catalytic removal of carbon monoxide from a hydrogen-containing gas conducted in a reactor as claimed in any one of claims 1 to 8.

11. A process as claimed in claim 10 wherein the hydrogen-containing gas is a reformate gas mixture.

Fig.1.

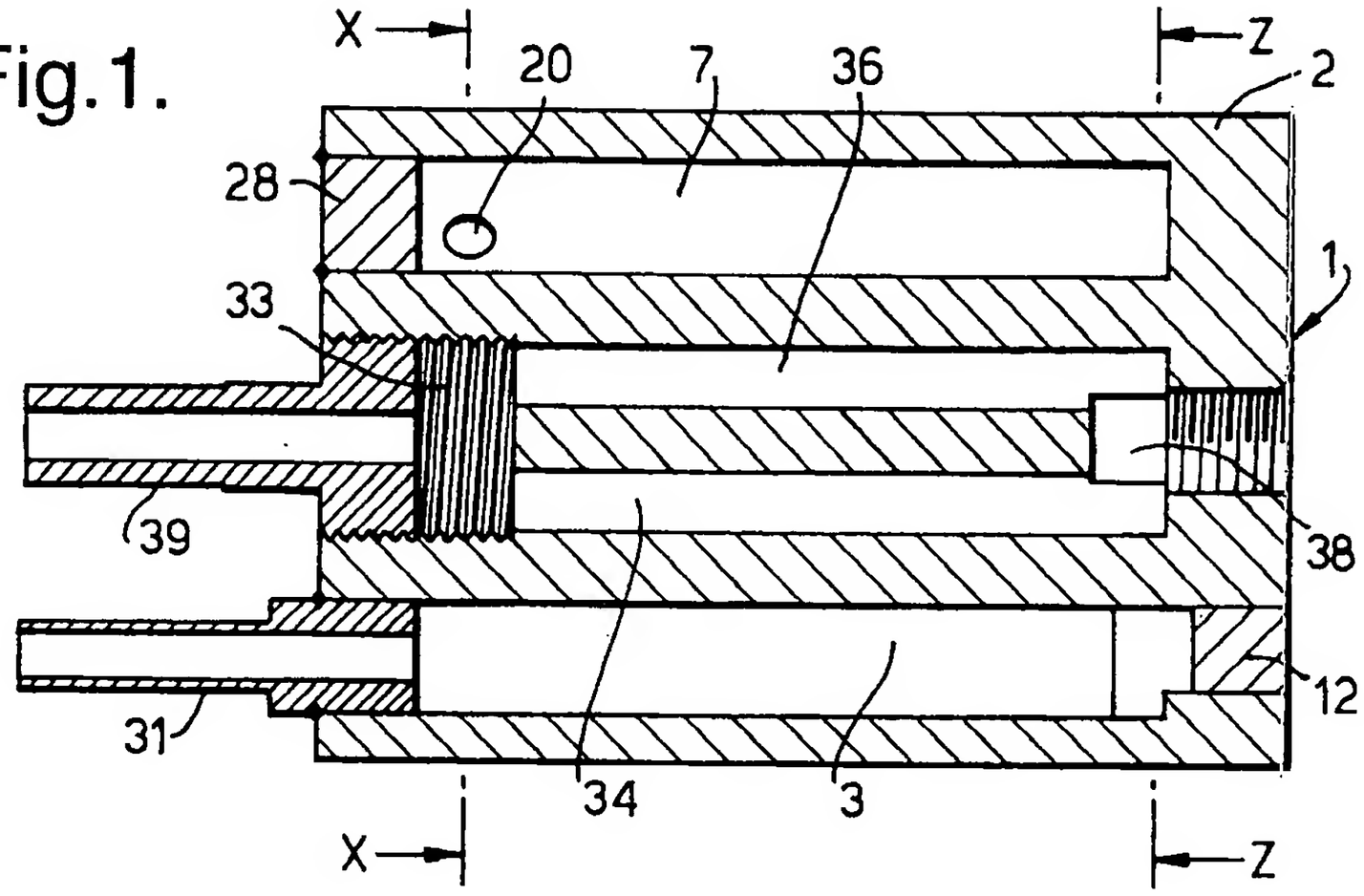


Fig.2.

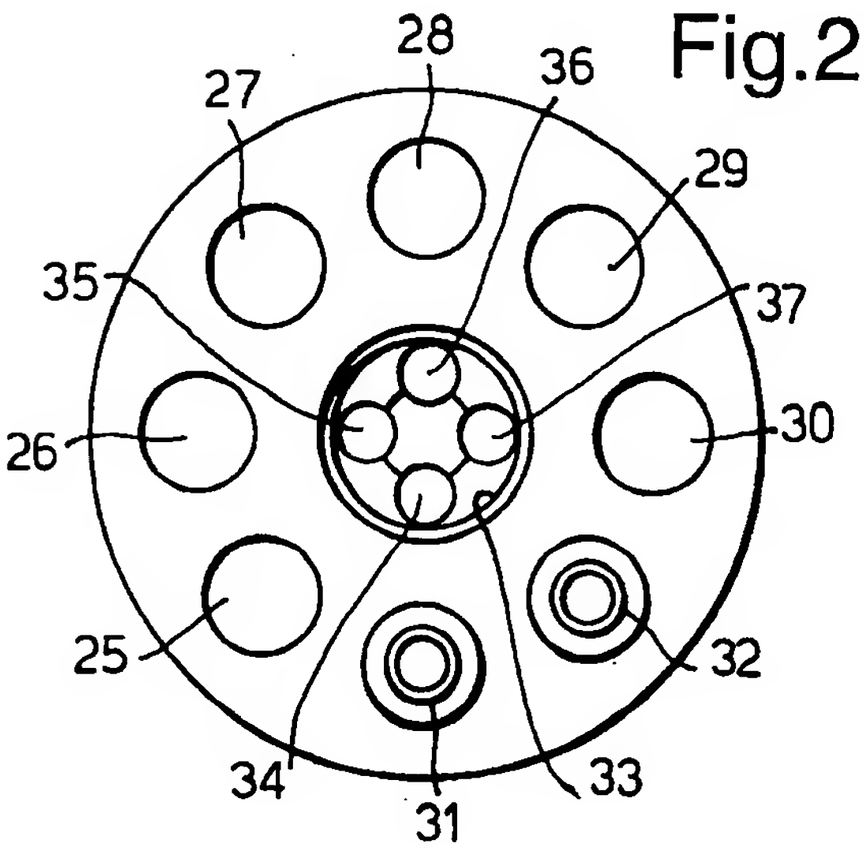


Fig.3.

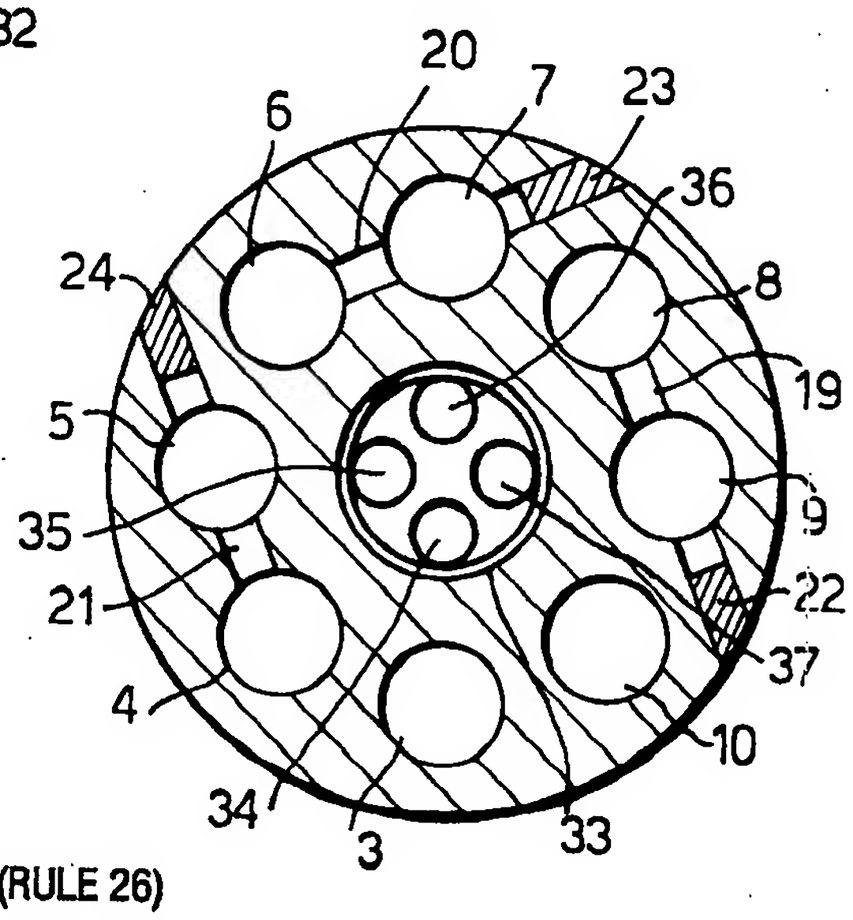


Fig.4.

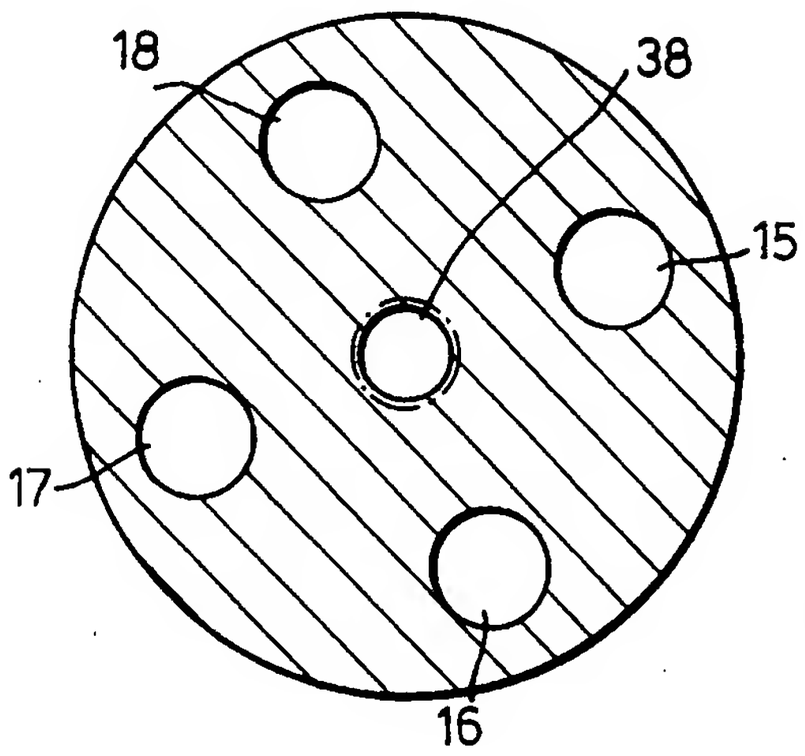


Fig.5.

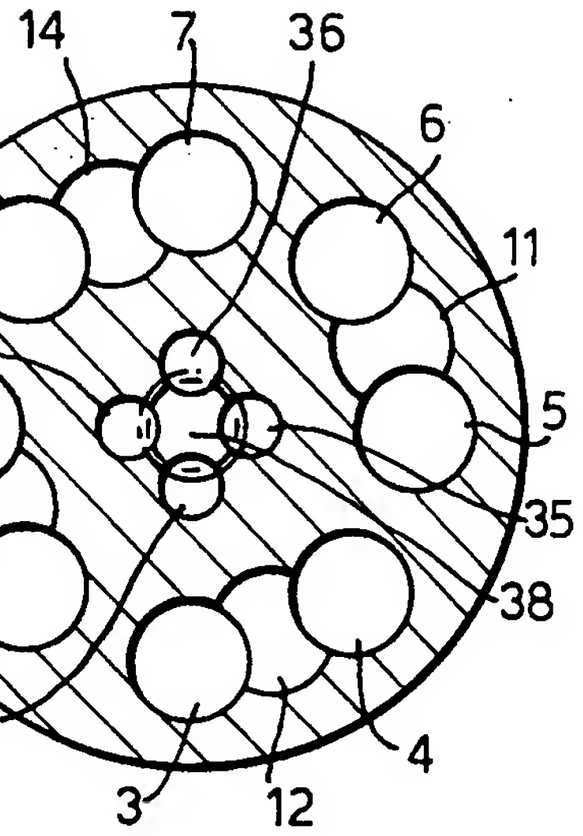
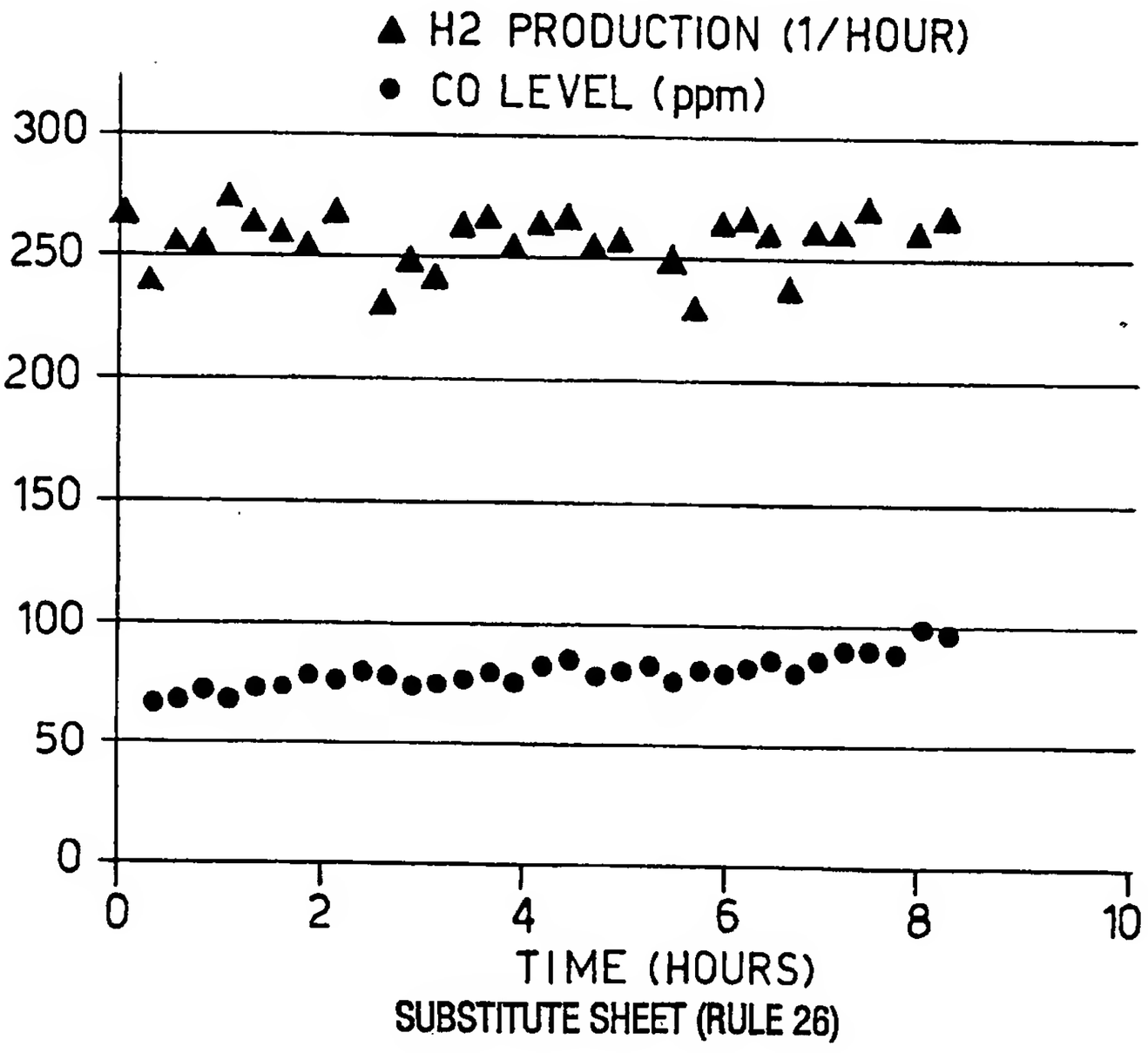


Fig.6.



INTERNATIONAL SEARCH REPORT

Internatio Application No
PCT/GB 98/01677

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J8/06 H01M8/06 C01B3/58

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J H01M C01B

Documentation searched other than minimumdocumentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 1 223 895 A (CANADIAN PATENTS DEV) , 7 July 1987 see page 4, line 3 - page 5, line 17 see page 8, column 17 - page 12, column 38; figures 1-4 ---	1-4,7-9
Y	US 4 371 500 A (PAPINEAU RONALD I) 1 February 1983	1-4,7-9
A	see column 2, line 42 - column 4, line 49 see column 6, line 9 - line 26 see column 5, line 48 - column 7, line 51 see column 13, line 17 - column 14, line 55; figures 1-4 ---	5

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 328 (C-621), 24 July 1989 & JP 01 107842 A (MITSUBISHI HEAVY IND LTD), 25 April 1989 see abstract	1
A	WO 93 19005 A (INT FUEL CELLS CORP) 30 September 1993 see claims 1-16	10,11
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Information on patent family members

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